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A MICROWAVE-INDUCED ARGON PLASMA SYSTEM SUITABLE FOR TRACE ANALYSIS

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In recent years there has been interest in the development of non-flame cells for spectroscopic analysis, *e.g.* the L'vov furnace[1], Massmann furnace[2], carbon filament atom reservoir[3] and platinum loop devices[4]. These have been shown to be valuable when the liquid sample available for analysis is too small for conventional pneumatic nebulising systems and when dilution results in concentrations below the detection limit. Non-flame cells, however, generally cannot be used for emission purposes because they lack the excitation energy necessary. In consequence, most emission studies have been concerned with the use of high-frequency or microwave-excited inert or diatomic gas plasmas[5-9] as an alternative to the use of flames. The main advantages of these systems are the high electronic excitation temperature (as high as 10,000°K) and the presence of an inert gas atmosphere which tends to preclude the formation of stable species such as metal oxides and hydroxides. However, in most instances, as with the use of flames, it is necessary to use conventional nebuliser systems for sample introduction, which reduces the detection limits obtained with most plasma systems.

The use of alternative methods of sample introduction has been suggested by Cooke *et al.*[10] and more recently by Runnels and Gibson[11], who both used low-powered, microwave-induced plasmas. In the former method, organic species eluted from a gas chromatographic column were introduced into the plasma cell; in the latter, excitation of mostly organometallic species was obtained in a plasma stream following volatilisation of a film of material from a heated platinum filament. However, the spectral measurements must be made through a quartz cell or tube which is subject to corrosion and plating-out of the elements of interest. In addition, we have found that when the procedure described by the latter workers is used, the plasma stability and analytical sensitivity depend on the solvent used.

The method described in this paper utilises a simple low-powered, microwave-induced argon plasma supported at the mouth of a quartz tube which is in turn connected to a platinum or tungsten loop[4] sample introduction device. The system provides a sensitive emission source for a wide range of elements and is suitable for very small sample volumes. In addition, a simple amplifier/integrator detection system is described which is capable of following the weak and transient emission signals received at the photomultiplier.

EXPERIMENTAL

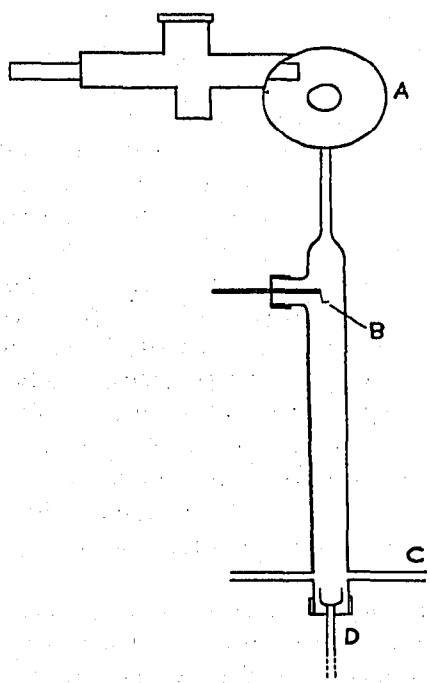
Plasma system

The microwave-induced argon plasma system is depicted in Fig. 1. Microwave energy (2450 ± 25 MHz) was derived from a "Microton 200"-microwave generator (Electro-Medical Supplies, Wantage, England) and coupling was via an Evenson type 1/4 λ resonant cavity (Electro-Medical Supplies 214 L). The radiation emitted from the plasma after sample volatilisation from the platinum or tungsten loop was viewed by means of a Unicam SP900 spectrophotometer with an EMI 9601B photomultiplier. The read-out unit normally incorporated in the instrument was by-passed in favour of the more rapid amplifier/integrator unit described below.

In the initial experiments a platinum loop was utilised to support the liquid sample and emission from cadmium (at 228.8 nm) was selected in order to optimise the various experimental parameters of the system.

Electronic read-out

Weak and transient light signals such as those obtained in the system outlined in this manuscript cannot be recorded by conventional d.c. amplification techniques common to most spectrophotometers. Normally the response time of the electronic



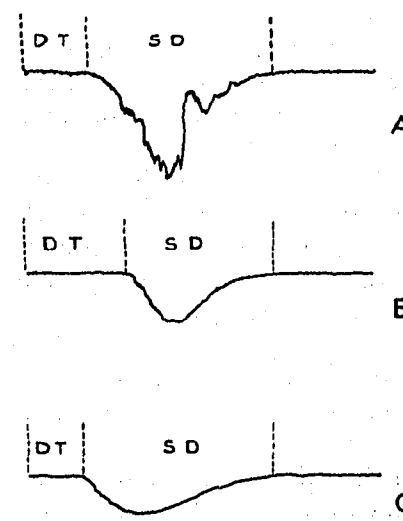


Fig. 1. Plasma cell and microwave cavity. (A) Microwave cavity, (B) platinum or tungsten loop, (C) gas inlets, (D) sample cup.

Fig. 2. Effect of argon flow rate on cadmium emission signal profile. Argon flow rate 2.5 l min^{-1} (A); 1.8 l min^{-1} (B); < 1.6 l min^{-1} (C). DT, delay time; SD, signal duration.

circuitry is high (approaching or even longer than the lifetime of the signal) which results in poor reproducibility and detection limits[12]. Figure 2 shows typical "pulses" of emission produced when a cadmium sample is vaporised from a platinum loop and is allowed to enter the plasma region. The radiation emitted at 228.8 nm was recorded via the spectrophotometer photomultiplier, the output of which was connected directly to a storage oscilloscope. These traces can be photographed and evaluated at a later date, but this is time-consuming and unnecessary. The emission signal is not always perfectly Gaussian in shape and integration of the total signal is the most obvious method. In such instances, the more commonly encountered spectroscopic apparatus utilising direct potentiometric recorder peak-height measurement would give poor reproducibility because of the relatively large response times of the recorder and amplifier circuits.

The rapid electronic amplifier/integrator described is capable of measuring this type of signal and the use of this or similar circuitry should be encouraged whenever transient signals or signals with a lifetime approaching that of the measuring system are encountered.

The dynode chain of the EMI 9601B photomultiplier present in the spectrophotometer was connected to negative EHT supply (*ca.* 1.0 kV) and the output was connected directly to the amplifier/integrator shown in Fig. 3, which was in turn connected to a Servoscribe potentiometric recorder.

Operating procedure

Allow about 20 min before making a series of measurements to permit stabilisation of supply and circuit. With switch S1 in position 1 (see Fig. 3), set up the first operational amplifier (OA1) for voltage and current trim. With the 5 kΩ potentiometer at the earth end of its track, adjust RV1 until there is 0 V at the output. (This can be determined with the Servoscribe recorder on the 2-mV range.) When this is achieved, the first operational amplifier is current-trimmed. Select the voltage trim ($R_{T_1} + R_{T_2}$) according to the value suggested by the manufacturer.

With S1 in position 2 and S2 in position 1, trim the second operational amplifier (OA2) as before by adjusting the helipot RV2.

If the off-sets have been correctly adjusted, S1 can be moved now to position 3 with readjustment of any trims provided there is no input current. The unit now operates as an amplifier with a gain of × 100. With switch S2 in position 2, the unit integrates the input signal after a gain of × 10 (due to OA1). The capacitor in the feedback loop of the OA2 charges at a rate proportional to the input voltage such that

$$E_{\text{output}} = -(RC)^{-1} \int_0^t E_{\text{in}} \, dt.$$

Thus for a 10-V output, 50 mV would have to be applied at the input for 1 sec.

The output voltage can be reset by pressing the reset button which discharges the capacitor.

Before each series of measurements the dark current from the photomultiplier tube must be offset. This is achieved by operating the OA1 in a differential mode and offsetting the positive input with the 5 kΩ preset such that with S1 in position 3 ans S2 in position 1 there is 0 V output. This means that the integrator, when S2 is in position 2, does not integrate the dark current, but only integrates the signal pulse. The zero can

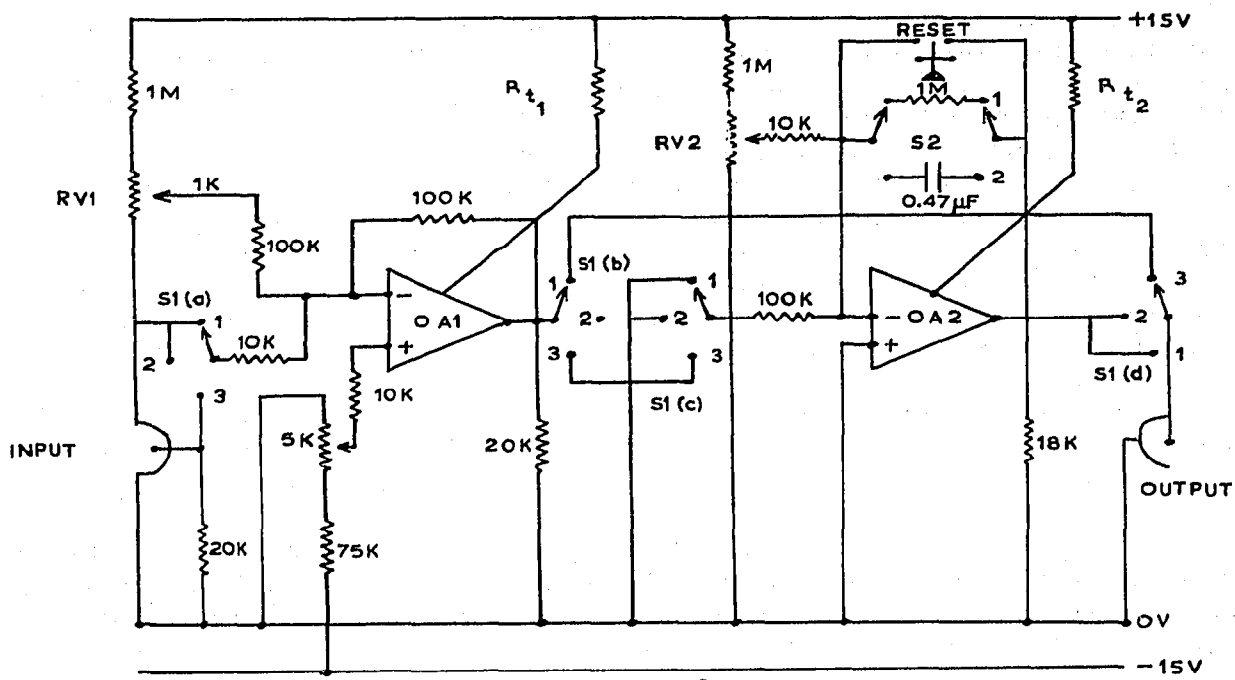


Fig. 3. Amplifier/integrator circuit:
OA1 = operational amplifier no. 1 } Philbrick PF85AU
OA2 = operational amplifier no. 2 }
S1 = switch no. 1—3 way 4 pole
S2 = switch no. 2—2 way 4 pole
RV1 = current off-set
RV2 = integrator off-set
Resistors, 0.5 W Hystab (Radiospares Ltd.)
Power supply, −15, 0, +15 V, Coutant OA10 stabilised supply unit.

be accurately trimmed before each reading by using the helipot RV2 to ensure integration is giving zero output. Once the radiation pulse has been recorded the output voltage is steady until the reset button is pushed.

The cost of the electronic system is very low, but the use of more expensive chopper-controlled operational amplifiers would eliminate many of the trimming and resetting operations described above.

The plasma cell

The plasma cell was constructed in transparent quartz from a piece of 8-mm (internal diameter) tubing *ca.* 10 cm in length with a jet fused into one end of it. The gas inlets were attached at the lower end, and a third part just below the fused jet allowed the platinum or tungsten loops to be introduced via a PVC plug. Dimensions were not found to be very critical except in the case of the jet which should be 2-mm internal diameter and sufficiently long to give laminar gas flow at the orifice. If the jet is too short, the plasma will be unstable and difficult to ignite. It was not possible to make the jet diameter equal to the diameter of the plasma (see below) because the gas velocity was then too great for the plasma to be ignited. Use of a 2-mm jet, however, caused the plasma to wander somewhat and hence change its position relative to the spectro-

photometer slit. Because of the different rates of diffusion of ions and electrons, plasmas in general have a negative sheath and a positive core. It was hence possible to solve the problem by securing to the jet a 15-mm length of 1-mm steel rod such that it was opposite the centre of the slit and parallel to it. The plasma induces a positive region within the steel rod and is thus attracted to it and held parallel to the slit. A pyrex sample cup (minimum capacity 20 μl) was sealed onto a greased glass rod and mounted into the main tube via a PVC plug; this allows the cup to be slid up and down so that the sample solution may be supplied to the loop. The diameter of the cup must be small enough so that gas is allowed to pass in its raised position without quenching the plasma. Alternatively, the liquid sample may be introduced with a syringe.

The plasma

The main body of the plasma was formed above the jet orifice so that plating out and devitrification problems encountered when the plasma is operated within a quartz tube were eliminated. We have found this to be a particularly difficult problem which cannot readily be solved by other methods. Under the recommended experimental conditions (see below) a short section of the plasma (*ca.* 2 mm) remained in the tube whilst a stable plasma pencil some 20 mm in length and 1.0 mm in diameter extended beyond the orifice. The plasma was formed by first tuning the cavity to minimum reflected power (with a reflected power meter) and then by initiating with a "Tesla" vacuum tester.

Sample loops

For most of the studies reported here, loops were made from 10-mm lengths of 0.1-mm diameter platinum wire. The loops formed resembled an ellipse with a major axis of 0.86 mm and a minor axis of 0.62 mm.

It was found that such a loop when just dipped into aqueous solution picked up a sample volume of *ca.* 0.12 μl which is in the form of a surface tension film with reproducible dimensions. The measurement was made by taking ten samples from a solution containing 1000 μg Cd ml^{-1}, washing them into a 10-ml volumetric flask and analysing the resulting solutions by atomic absorption spectroscopy. Several loops were made and their sampling volumes were found to range between 0.1 and 0.15 μl.

The aqueous film was evaporated first by the passage of *ca.* 0.1 A d.c. (via a 4.5 V battery and variable resistance); during this process the plasma became less stable and shorter in length. Then the current was increased to *ca.* 1.9 A which caused the compound remaining on the loop to vaporise and pass into the plasma region. Tungsten loops formed from 0.1-mm tungsten wire were used when a higher volatilisation temperature than could be achieved with platinum was required.

Optimal operating conditions

Argon flow rate. Gas flow rate was found to be the most critical factor influencing plasma stability and therefore a careful examination of its effect was made. An oscilloscope with a storage facility was used to observe the signal profile obtained when a sample containing 10 μg Cd ml^{-1} was vaporised into the plasma at varying gas flow rates. Provision of a calibrated time base on this instrument also enabled the delay time (from the switch-on of the loop current to the beginning of the signal profile) and signal duration to be measured. With an argon flow rate of 2.95–2.10 l min^{-1}, the

plasma was unstable owing to turbulence in the gas jet. Figure 2A shows a typical signal profile under these conditions; the shape is non-Gaussian in nature having a linear growth and exponential decay. The turbulence of the plasma is reflected in the positive and negative fluctuations superimposed on the main profile. In this instance the delay time was 75 msec and the signal duration 225 msec.

The plasma was stable when the argon flow rate was between 2.10 and 1.64 l min^{-1} and was easy to initiate. The profile obtained (Fig. 2B) is smoother than before and slightly flattened at the bottom. This indicates that the sample vaporisation rate and the rate at which the argon is carrying the vapour to the plasma are approximately equal. The delay time was again 75 msec and the signal duration was slightly longer at 250 msec.

Below 1.64 l min^{-1} the plasma rapidly decreased in length and was finally quenched at a flow rate of *ca.* 1.03 l min^{-1}. Plasmas in general are sensitive to the introduction of molecular species and the rate of sample introduction must be low to

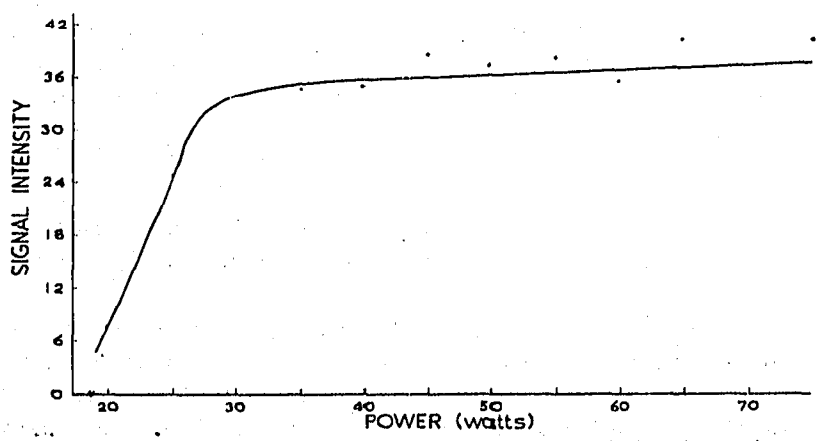


Fig. 4. Effect of microwave power on cadmium emission intensity.

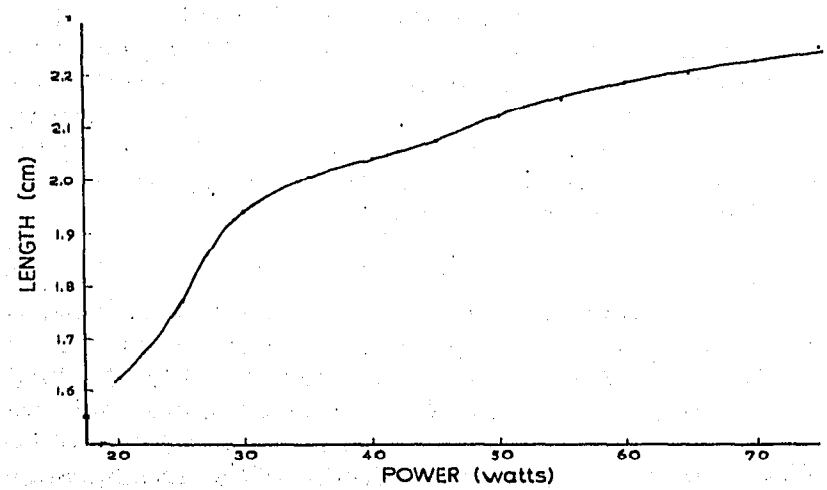


Fig. 5. Effect of microwave power on plasma length.

avoid quenching the plasma. In the system described here (Fig. 2C) a period of ca. 5 sec was required to evaporate the water under normal conditions; a much longer period was necessary at low argon flow rates. In this instance, the signal profile was very shallow along its bottom edge indicating a lower rate of sample introduction to the plasma. The delay time was 90 msec, but the signal duration remained at 250 msec. A flow rate of 1.85 l min^{-1} was chosen as optimum because it resulted in a stable plasma and a reproducible signal profile.

Optimal microwave power. The optimal microwave power was determined with the argon flow rate set at 1.85 l min^{-1}. A stable plasma could be maintained at microwave powers ranging from 20 to 75 W. Samples containing 0.1 μg Cd ml^{-1} were vaporised into the plasma at varying powers within this range and the resulting signals were recorded on a Servoscribe potentiometric recorder (Fig. 4). It was noted that the plasma increased in length with increasing microwave power; Fig. 5 shows a plot of microwave power *versus* plasma length. The graph shows that at about 35 W the length of the plasma reaches 20 mm and then just fills the entrance slit (20 mm long) of the spectrophotometer used. It was therefore concluded that the increase in plasma dimensions was responsible for the steep rise in the signal/power curve (Fig. 4) and not an increase in the translational or electronic excitation temperature. The coupling of the microwave energy to the plasma is not 100% efficient and therefore increasing the input power above the level required to give a stable plasma results in higher reflected powers and a slightly longer plasma, but no increase in the emission signal. The optimal microwave power was selected at 40 W because it represented a point on the plateau of the signal/power curve.

Occurrence of intensity antinodes in the plasma. The entrance slit was blocked except for a 2-mm square portion in the centre to view the plasma. The emission intensities of the argon background and of cadmium signals were then observed at different plasma heights. Identical curves were obtained for each, showing a large maximum opposite the central electrode and a much smaller and less pronounced maximum near the edge of the cavity approximately 9 mm below the first. It is thought that these maxima occur at positions where the electric field intensity within the cavity is greatest.

RESULTS

Analytical working curve for cadmium

Analytical-grade chemicals and deionised water were used in the preparation of all solutions. Ten samples at each concentration examined were vaporised into the plasma and the readings at 228.8 nm were averaged. The slope of the log/log curve (Fig. 6) is unity and the normal analytical working curve is linear over the concentration range 0.01–5.00 μg Cd ml^{-1}. It was not possible to study concentrations above 5.00 μg Cd ml^{-1}, because the capacitor used in the integrator was almost fully charged at this level. Normally this problem could be avoided by reducing the spectral band pass of the monochromator, but this also reduces the background radiation from the plasma, which necessitates changing the backing-off potentiometer in the amplifier system. Curves constructed without using the integrator were not of a reproducible shape and were non-linear, the signal increasing approximately 4-fold for a 1000-fold increase in concentration. The slit width was set at 0.1 mm for most of the experiments reported here. Solutions containing 0.002 μg Cd ml^{-1} were detected with the photo-

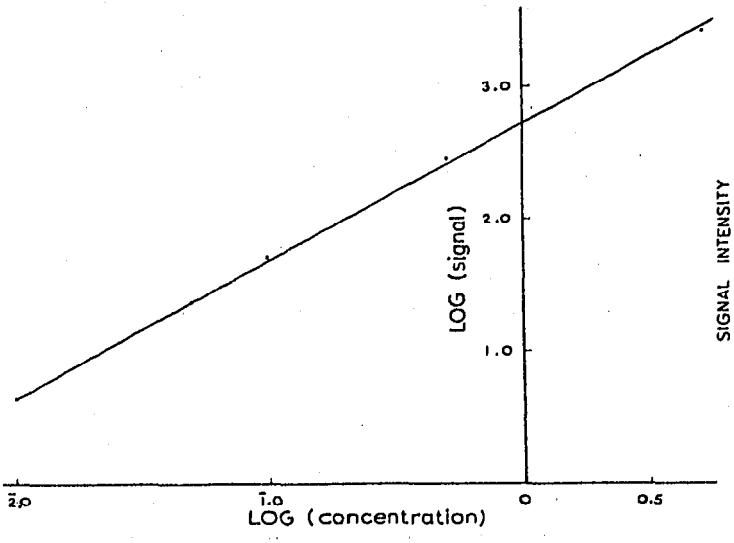


Fig. 6. Log–log analytical working curve for cadmium.

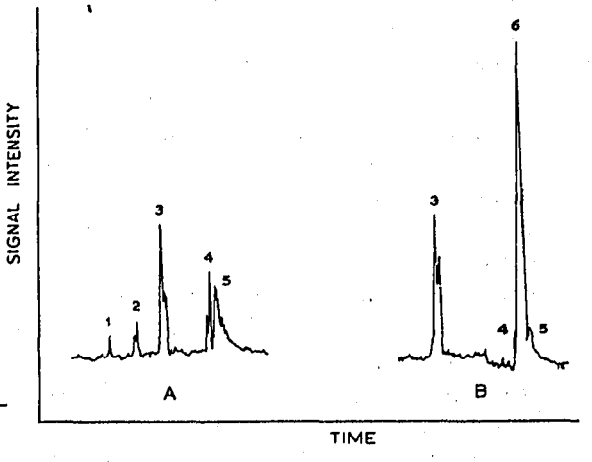


Fig. 7. Arsenic interference on cadmium emission. A: (1, 2, 3) Arsenic signal profiles at room temperatures, (4, 5) arsenic signal profiles with loop at red-heat. B: (3, 4, 5) As above in A, (6) cadmium signal profile with loop at red-heat.

multiplier EHT supply set to its maximum value of 1.2 kV. This represents an absolute detection limit for cadmium of $2 \cdot 10^{-13}$ g. Precision data were obtained by analysing thirty solutions containing 0.25 μg Cd ml^{-1}. The relative standard deviation obtained was 10% which can be attributed to three factors:

(i) drift by the operational amplifiers which were not chopper-stabilised,
(ii) variation in the quantity picked up by the loop, and
(iii) variation in the proportion of sample entering the plasma (the plasma pencil did not completely fill the 2.0-mm jet orifice).

It is thought that improvements with respect to factors (i) and (ii) in particular should considerably increase the precision of the method.

Interferences

Spectral interferences. Solutions containing 0.25 μg Cd ml^{-1} together with various other elements present in 1000-fold molar amounts were studied. The strongest spectral interference associated with cadmium comes from the 228.812-nm direct line emission from arsenic. The solutions of arsenic were prepared by dissolving arsenic trioxide in 20% (v/v) hydrochloric acid and then diluting to volume with water. When a sample containing both cadmium and arsenic was vaporised rapidly by switching the current directly to 1.9 A, a large positive interference was observed. However, it was found subsequently that emission peaks were observed without heating the loop and that further peaks could be obtained by increasing the current to its maximum (1.9 A) over a period of time. Figure 7 shows two traces (unintegrated) which illustrate the effect of adding arsenic to a cadmium solution. The ratio of concentrations was

TABLE I

LIMITS OF DETECTION FOR VARIOUS ELEMENTS

Element	*Wavelength (nm)*	*Loop material*	*Detection limit (g)*	*Detection limit (p.p.m.) for 0.12-μl sample*
Zinc	213.85	Pt	$8.0 \cdot 10^{-11}$	0.67
Antimony	252.85	Pt	$5.0 \cdot 10^{-10}$	4.60
Selenium	203.98	Pt	$4.0 \cdot 10^{-10}$	3.24
Arsenic	228.81	Pt	$4.2 \cdot 10^{-11}$	0.35
Lead	261.41	Pt	$1.2 \cdot 10^{-10}$	1.0
Cadmium	228.81	Pt	$2.0 \cdot 10^{-13}$	0.0017
Iron	248.32	Pt	$3.0 \cdot 10^{-10}$	2.5
Iodine	206.16	Pt	$1.2 \cdot 10^{-9}$	10.0
Copper	217.89	W	$1.2 \cdot 10^{-10}$	1.0
Boron	249.77	W	$1.2 \cdot 10^{-10}$	1.0
Beryllium	234.86	Pt	$1.2 \cdot 10^{-10}$	1.0
Mercury	253.65	Pt	$1.6 \cdot 10^{-11}$	0.13

chosen so that peaks caused by both arsenic and cadmium were easily discernible. When a solution containing 10 μg As ml^{-1} alone was placed on the loop peaks 1, 2 and 3 (Fig. 7A) were observed after *ca.* 40 sec. Then the current was increased steadily to its maximum of 1.9 A; peaks 4 and 5 were observed when the current reached 1.5 A and the loop was just below red-heat (*ca.* 500° K). The separation of peaks 1–2 and 2–3 is *ca.* 3 sec each, and the separation of peaks 3–4 and 4–5 depends on the rate at which the loop is heated. Figure 7B shows that cadmium is vaporised (peak 6) at a temperature between that of the arsenic species (represented by peaks 4 and 5). This investigation shows that under suitable conditions the system might be used not only for the determination of total concentration of an element, but also for the determination of the different species present.

No interference was observed from either cobalt or antimony, both of which exhibit emission close to 228.8 nm (Co at 228.781 nm and Sb at 228.898 nm) when present in a 1000-fold molar amount compared to cadmium. Cadmium solutions containing sodium ($\geqq$ *ca.* 5000 μg ml^{-1}) distorted the integrated emission reading owing to a light leak in the spectrophotometer used. Under these conditions sodium emission was observed visually for several minutes after the cadmium signal was received and the precision of the measurement was decreased slightly.

Chemical interferences. The effects of phosphate, silicate, aluminium and vanadium when present in 1000-fold molar amounts compared to cadmium were also investigated. Only vanadium, present in the form of ammonium metavanadate, was found to interfere, giving a 40% reduction in the expected signal intensity.

Application to other elements

Table I shows the limits of detection obtained with platinum or tungsten loops (as indicated) for a range of elements. As can be seen, the system is applicable to elements which are well known to form stable refractory oxides in flames. The most useful spectral region of measurement is below *ca.* 300.0 nm where the plasma background is lowest. In comparison to high-temperature flames the plasma background radiation

throughout the u.v./visible region of the spectrum is very low. Sheathing the plasma with argon reduces the background even further by removing the nitrogen and N–O bands appearing above *ca.* 300.0 nm. The system may also be used to monitor carbon emission at the 247.8-nm line and hence may have application in certain organic analyses.

In conclusion, the system described enables a highly sensitive analysis to be carried out on small volumes of liquid sample. Interferences in the case of cadmium were not serious, which is probably a result of the argon atmosphere surrounding the sample during all stages of the evaporation and excitation stages. The system is sufficiently versatile so that by modifying the method of sample introduction it should be possible to examine vaporised solids and gas mixtures. Future work is directed towards extending the field of application and to the use of photon counting as a read-out technique to improve the precision and detection limits.

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SUMMARY

A non-flame cell utilising a microwave-induced argon plasma at atmospheric pressure is described for emission spectroscopic purposes. The system operates at a microwave power of *ca.* 40 W (2450 MHz) and requires the use of only minute liquid samples. Optimal operating parameters are investigated and the method is tested on a range of elements. In addition, the use of a high-speed operational amplifier/integrator is described which is capable of following the weak and transient signals common to non-flame methods of atomisation.

RÉSUMÉ

On décrit un dispositif de cuve pour mesures spectroscopiques d'émission sans flamme. Ce système ne nécessite que de faibles quantités d'échantillon liquide. On examine divers paramètres. On propose l'utilisation d'un amplificateur permettant de suivre les signaux faibles et fugitifs communs aux méthodes d'atomisation sans flamme.

ZUSAMMENFASSUNG

Für emissionsspektroskopische Zwecke wird eine flammenlose Zelle mit einem mikrowellenerregten Argon-Plasma von Atmosphärendruck angewendet. Die Mikrowellenleistung beträgt *ca.* 40 W (2450 MHz); es sind nur sehr kleine flüssige Proben erforderlich. Die optimalen Bedingungen werden untersucht; die Methode wird mit einer Reihe von Elementen geprüft. Zusätzlich wird die Anwendung eines sehr schnellen Verstärker-Integrators beschrieben, der den schwachen und kurzzeitigen Signalen folgen kann, die bei flammenlosen Atomisierungsmethoden erhalten werden.

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